METHODS OF CEMENTING IN SUBTERRANEAN FORMATIONS USING CRACK RESISTANT CEMENT COMPOSITIONS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to subterranean cementing operations, and more particularly, to methods of cementing in subterranean formations using cement compositions that autogenously cure voids that may form in such cement compositions.

[0002] Hydraulic cement compositions are commonly used in subterranean operations, particularly subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipe strings, such as casings and liners, are cemented in well bores. In performing primary cementing, hydraulic cement compositions are pumped into the annular space between the walls of a well bore and the exterior surface of the pipe string disposed therein. The cement composition is permitted to set in the annular space, thereby forming an annular sheath of hardened, substantially impermeable cement therein that substantially supports and positions the pipe string in the well bore and bonds the exterior surfaces of the pipe string to the walls of the well bore. Hydraulic cement compositions also are used in remedial cementing operations such as plugging highly permeable zones or fractures in well bores, plugging cracks and holes in pipe strings, and the like.

[0003] Once the cement sets, voids may be present in the resultant set cement sheath. These voids may result from a number of possible causes, such as from the occurrence of a chemical reaction during hydration, from stresses imparted onto the cement composition caused by subterranean operations, and/or from stress exerted by the environment. For example, where hydration occurs too rapidly, voids may result. Voids may form from pipe movements, pipe expansions, impacts, and/or shocks generated by drilling and other subterranean operations, that may occur simultaneously with the setting of the composition. In one instance, voids may form during subterranean operations from the use of expandable tubulars, such as pipes, pipe strings, casings, liners, and the like.

[0004] Voids in set cement sheaths are generally undesirable, *inter alia*, because they may lead to loss of zonal isolation, which may allow formation fluids to enter the well bore and/or well bore fluids to enter the formation. In an attempt to counteract this problem, various additives (*e.g.*, fibers and/or expansion additives) have been added to cement compositions.

However, such techniques may not prevent the formation of voids and thus can lead to a loss of zonal isolation.

SUMMARY OF THE INVENTION

[0005] The present invention relates to subterranean cementing operations, and more particularly, to methods of cementing in subterranean formations using cement compositions that autogenously cure voids that may form in such cement compositions.

[0006] In one embodiment, the present invention provides a method of cementing in a subterranean formation penetrated by a well bore comprising the steps of: placing a cement composition into the well bore, wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component having a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; and allowing the second cementitious component to set after a delay period.

[0007] In other embodiments, the present invention provides a method of cementing in a subterranean formation penetrated by a well bore comprising the steps of: placing a cement composition into the well bore, wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component comprising microencapsulated cement particles, wherein the second cementitious component has a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; and allowing the second cementitious component to set after a delay period.

[0008] In other embodiments, the present invention provides a method of cementing an expandable tubular in a subterranean formation penetrated by a well bore comprising the steps of: placing the expandable tubular into the well bore; placing a cement composition into the well bore wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component having a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; expanding the expandable tubular; and allowing the second cementitious component to set after a delay period.

[0009] In other embodiments, the present invention provides a method of cementing an expandable tubular in a subterranean formation penetrated by a well bore comprising the steps of: placing the expandable tubular into the well bore; placing a cement composition into the well bore wherein the cement composition comprises a first cementitious

component having a first set time and a second cementitious component comprising microencapsulated cement particles, wherein the second cementitious component has a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; expanding the expandable tubular; and allowing the second cementitious component to set after a delay period.

[0010] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments, which follows.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0011] The present invention relates to subterranean cementing operations, and more particularly, to methods of cementing in subterranean formations using cement compositions that autogenously cure voids that may form in such cement compositions. As used herein, the phrase "cure voids" refers to the ability of the cement compositions of the present invention to fill, partially fill, and/or obstruct at least one void that may form in such cement compositions.

[0012] The cement compositions used in the methods of the present invention generally comprise water, a first cementitious component having a first set time, and a second cementitious component having a second set time that is delayed relative to the set time of the first cementitious component. It is understood that the cement compositions of the present invention may be foamed or unfoamed or may comprise other means to reduce their densities. Other additives suitable for use in subterranean well bore cementing operations also may be added to these cement compositions as desired. A cement composition useful in the methods of the present invention is described in U.S. Patent No. 6,565,644, the disclosure of which is incorporated herein by reference.

[0013] The water present in the cement compositions of the present invention can be fresh water, salt water (*e.g.,* water containing one or more salts dissolved therein), brine (*e.g.,* saturated salt water), or seawater. Generally, the water can be from any source, provided that it does not contain an excess of compounds, *e.g.*, dissolved organics, that may adversely affect other components in the cement composition. The water may be present in an amount sufficient to form a pumpable slurry. Generally, the water is present in the cement compositions in an amount in the range of from about 25% to about 180% by weight of the cement ("bwoc") therein.

[0014] Any hydraulic cement that is suitable for use in subterranean applications may be suitable for use as the first cementitious component. A variety of hydraulic cements are suitable for use, including those comprised of calcium, aluminum, silicon, oxygen, and/or sulfur, which set and harden by reaction with water. Such hydraulic cements include, but are not limited to, Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, soil cements, calcium phosphate cements, high alkalinity cements, and mixtures thereof.

[0015] In an exemplary embodiment, at least one void may form during the setting of the first cementitious component. Voids may form during the setting of the first cementitious component, *inter alia*, from the occurrence of a chemical reaction during hydration, from stresses imparted onto the cement composition caused by subterranean operations, and/or from stresses exerted by the environment. In an exemplary embodiment, at least one void is due to at least the use of an expandable tubular.

[0016] Generally, the second cementitious component of the cement compositions of the present invention may be any suitable cement having a set time that is delayed relative to the set time of the first cementitious component. For example, in one embodiment, the second cementitious component will not begin to hydrate until after a delay period. In an exemplary embodiment, the delay period is at least a few hours to a few days after the bulk (*e.g.*, at least over one half thereof) of the first cementitious component has hydrated. Among other things, the delayed set of the second cementitious component may cure at least one void that may form during the setting of the first cementitious component.

[0017] In an exemplary embodiment, the second cementitious component may comprise microencapsulated cement particles designed so as to be time-released, thereby delaying the set of such microencapsulated cement particles for a delay period. The microencapsulated cement particles present in the cement compositions, in certain embodiments, may comprise any hydraulic cement that is suitable for use in subterranean applications. A variety of hydraulic cements are suitable for use including those comprised of calcium, aluminum, silicon, oxygen, and/or sulfur, which set and harden by reaction with water. Such hydraulic cements include, but are not limited to, Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, soil cements, calcium phosphate cements, high alkalinity cements, and mixtures thereof. Further, in an exemplary embodiment, the hydraulic cement may be an expansive hydraulic cement. A suitable expansive hydraulic cement is described in U.S. Patent No. 6,457,524, the disclosure of which is incorporated herein by reference.

[0018] Further, the microencapsulated cement particles may comprise conventional particle size cement, fine particle size cement, ultra-fine particle size cement, or mixtures thereof. In an exemplary embodiment, the microencapsulated cement particles may comprise an ultra-fine particle size cement having particle diameters not greater than about 30

microns, preferably not greater than about 17 microns, and still more preferably not greater than about 11 microns. Ultra-fine particle size cement generally has a particle size distribution where 90% percent of the particles have a diameter not greater than about 25 microns, preferably not greater than about 10 microns, and more preferably not greater than about 4 microns; and 20 percent of the particles have a diameter not greater than about 5 microns, preferably not greater than about 3 microns, and more preferably not greater than about 2 microns. Suitable examples of ultra-fine particle size cement are described in U.S. Patent Nos. 5,086,850; 5,121,795; 5,123,487; 5,127,473; and 5,238,064, the relevant disclosures of which are incorporated herein by reference. An example of a suitable ultra-fine particle size cement is "MICRO MATRIX®" cement, which is commercially available from Halliburton Energy Services, Duncan, Oklahoma.

[0019] The microencapsulated cement particles may be prepared, in certain embodiments, using any suitable encapsulation methodology, whereby the microencapsulated cement particles may be released into the cement composition after a delay period. Generally, the microencapsulation of the second cementitious component involves at least one coating of a degradable material. Exemplary encapsulation methodologies are described further in U.S. Patents Nos. 5,604,186; 6,357,527; 6,444,316; 6,527,051; and 6,554,071, the relevant disclosures of which are incorporated herein by reference. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate encapsulation methodology to use for a chosen application.

[0020] The coating applied to the microencapsulated cement particles in certain embodiments may be selected from a number of different suitable degradable materials capable of preventing incorporation of the microencapsulated cement particles into the cement composition until after a desired delay period. In an exemplary embodiment, the coating should not substantially degrade for at least six hours in a high pH environment.

[0021] It is understood that when degradable materials are used as a coating as described herein, such degradable materials are capable of undergoing an irreversible degradation downhole. The term "irreversible" as used herein means that the degradable material, once degraded downhole, should not recrystallize or reconsolidate while downhole, *e.g.*, the degradable material should degrade *in situ* but should not recrystallize or reconsolidate *in situ*. The terms "degradation" or "degradable" refer to both the two relatively extreme cases of hydrolytic degradation that the degradable material may undergo, *i.e.*, heterogeneous (or bulk

erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two. This degradation can be a result of, *inter alia*, a chemical or thermal reaction or a reaction induced by radiation.

[0022] In an exemplary embodiment, the degradable material comprises a degradable polymeric material. One should be mindful that the degradability of a polymer depends at least in part on its backbone structure. The physical properties of degradable polymeric materials depend on several factors such as the composition of the repeat units, flexibility of the chain, presence of polar groups, molecular mass, degree of branching, crystallinity, orientation, etc. For example, short chain branches reduce the degree of crystallinity of polymers while long chain branches lower the melt viscosity and impart, *inter alia*, elongational viscosity with tension-stiffening behavior. The properties of the coating utilized can be further tailored by blending, and copolymerizing it with another polymer, or by a change in the macromolecular architecture (*e.g.*, hyper-branched polymers, star-shaped, or dendrimers, etc.). The properties of any such suitable degradable polymeric materials (*e.g.*, hydrophobicity, hydrophilicity, rate of degradation, etc.) can be tailored by introducing select functional groups along the polymer chains. For example, poly(phenyllactide) will degrade at about 1/5th of the rate of racemic poly(lactide) at a pH of 7.4 at 55°C. One of ordinary skill in the art with the benefit of this disclosure will be able to determine the appropriate degradable polymeric material to achieve the desired physical properties of the coating.

[0023] Suitable examples of degradable materials that may be used in accordance with the present invention include but are not limited to those described in the publication of Advances in Polymer Science, Vol. 157 entitled "Degradable Aliphatic Polyesters" edited by A.-C. Albertsson, pages 1-138. Specific examples include homopolymers, random, block, graft, and star- and hyper-branched aliphatic polyesters. Polycondensation reactions, ring-opening polymerizations, free radical polymerizations, anionic polymerizations, carbocationic polymerizations, coordinative ring-opening polymerization, and any other suitable process may prepare such suitable polymers. Specific examples of suitable degradable materials include polysaccharides such as dextrans or celluloses; chitins; chitosans; liquid esters (*e.g.*, triethyl citrate); proteins (*e.g.*, gelatin); aliphatic polyesters; poly(lactides); poly(glycolides); poly(ε-caprolactones); poly(hydroxybutyrates); poly(anhydrides); aliphatic polycarbonates; ortho esters, poly(orthoesters); poly(amino acids); poly(ethylene oxides); and polyphosphazenes.

[0024] In choosing the appropriate degradable material, one should consider the degradation products that will result. These degradation products should not adversely affect other operations or components. The choice of degradable material also can depend, at least in part, on the conditions of the well, e.g., wellbore temperature. For instance, lactides have been found to be suitable for lower temperature wells, including those within the range of 60°F to 150°F, and polylactides have been found to be suitable for well bore temperatures above this range. Also, poly(lactic acid) may be suitable for higher temperature wells. Some stereoisomers of poly(lactide) or mixtures of such stereoisomers may be suitable for even higher temperature applications. Also, in some embodiments, it is desirable for the degradable material to degrade slowly over time as opposed to instantaneously.

[0025] Generally, the coating should release the microencapsulated cement particles to become incorporated within the cement composition after a desired delay period so that the set time of the second cementitious component is delayed relative to the set time of the first cementitious component. In at least one embodiment, the microencapsulation should prevent the microencapsulated cement particles from hydrating until they come into contact with water after their release from encapsulation. When the microencapsulated cement particles are released from encapsulation after the delay period, they hydrate so that the microencapsulated cement particles, among other things, cure at least one void formed during the setting of the first cementitious component. In an exemplary embodiment, the delay period is at least a few hours to a few days after the bulk (*e.g.*, at least over one half thereof) of the first cementitious component has hydrated.

[0026] In an exemplary embodiment, the second cementitious component should be present in the cement compositions of the present invention in a first cementitious component-to-second cementitious component weight ratio in the range of from about 50:50 to about 90:10. In an exemplary embodiment, the microencapsulated second cementitious material should be present in the cement compositions of the present invention in a first cementitious component-to-second cementitious component weight ratio in the range of from about 85:15 to about 90:10.

[0027] Optionally, in an exemplary embodiment, the second cementitious component may be combined with an expanding additive prior to microencapsulation, thereby allowing for the simultaneous microencapsulation of the expanding additive and the second cementitious component. In another exemplary embodiment, the cement compositions of the

present invention optionally may comprise an expanding additive that has been microencapsulated in a coating of a degradable material using encapsulation techniques as discussed above for microencapsulation of the second cementitious component. Examples of suitable expanding additives include, but are not limited to, aluminum powder, gypsum blends, and deadburned magnesium oxide. Suitable examples of expanding additives are described in U.S. Pat. Nos. 4,304,298; 4,340,427; 4,367,093; 4,450,010 and 4,565,578, the disclosures of which are incorporated herein by reference. Exemplary expanding additives comprising aluminum powder are commercially available under the tradenames "GAS-CHEK®" additive and "SUPER CBL" from Halliburton Energy Services, Duncan, Oklahoma. An exemplary expanding additive comprising a blend containing gypsum is commercially available under the tradename "MICROBOND" from Halliburton Energy Services, Duncan, Oklahoma. Exemplary expanding additives comprising deadburned magnesium oxide are commercially available under the tradenames "MICROBOND M" and "MICROBOND HT" from Halliburton Energy Services, Duncan, Oklahoma.

[0028] Furthermore, additional additives may be added to the cement compositions of the present invention as deemed appropriate by one skilled in the art, with the benefit of this disclosure. Examples of such additives include, *inter alia*, fly ash, silica compounds, fluid loss control additives, surfactants, dispersants, accelerators, retarders, salts, micas, fibers, formation conditioning agents, bentonite, microspheres, weighting materials, defoamers, and the like.

[0029] An example of a method of the present invention is a method of cementing in a subterranean formation penetrated by a well bore comprising the steps of: placing a cement composition into the well bore, wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component having a second set time this is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; and allowing the second cementitious component to set after a delay period.

[0030] Another example of a method of the present invention is a method of cementing in a subterranean formation penetrated by a well bore comprising the steps of: placing a cement composition into the well bore, wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component

comprising microencapsulated cement particles, wherein the second cementitious component has a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; and allowing the second cementitious component to set after a delay period.

[0031] Another example of a method of the present invention is a method of cementing an expandable tubular in a subterranean formation penetrated by a well bore comprising the steps of: placing the expandable tubular into the well bore; placing a cement composition into the well bore wherein the cement composition comprises a first cementitious component having a first set time, and a second cementitious component having a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; expanding the expandable tubular; and allowing the second cementitious component to set after a delay period.

[0032] Another example of a method of the present invention is a method of cementing an expandable tubular in a subterranean formation penetrated by a well bore comprising the steps of: placing the expandable tubular into the well bore; placing a cement composition into the well bore wherein the cement composition comprises a first cementitious component having a first set time and a second cementitious component comprising microencapsulated cement particles, wherein the second cementitious component has a second set time that is delayed relative to the first set time of the first cementitious component; allowing the first cementitious component to at least partially set; expanding the expandable tubular; and allowing the second cementitious component to set after a delay period.

[0033] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.